The Quantitative Methods for Fluorine

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THESIS

presented to the Faculty of the Graduate School of the University of Pennsylvania in partial fulfilment of the requirements for the degree of Doctor of Philosophy

BY

WILLIAM H. ADOLPH

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ACKNOWLEDGMENT.

The author desires to express his sincere thanks to Dr. Edgar F. Smith under whose direction and personal encouragement this study was undertaken.

INTRODUCTION.

The existing methods for the estimation of fluorine have been universally acknowledged to be unsatisfactory. Those which are in any sense satisfactory can only be employed under very special conditions. Indirect methods under some circumstances can be employed with acceptable results, but these are open to the influences of compensating errors. No fluoride absolutely insoluble under suitable analytical conditions has been found. Calcium fluoride is somewhat soluble and is decomposed by prolonged ignition. It is not a simple matter to account for all the fluorine in a silicate mineral.

The literature upon the analytical determination of fluorine is extensive. Many of the methods in the literature present results which have never been successfully confirmed. Some of the methods suggested have never been applied to actual determinations of fluorides, but these should, however, not be set aside for they contain much of ingenious suggestion. In the hope that perhaps a review of the existing methods and schemes proposed for estimating fluorine would disclose their inherent weakness and point to the discovery of modifications leading to distinct improvements or a distinctly new method, the present study was undertaken.

SYSTEMATIC BIBLIOGRAPHY.

The methods for fluorine fall naturally into four main groups: (1) Those depending on the precipitation and weighing of calcium fluoride, a process which can be applied to all substances containing fluorine; (2) those involving the expulsion of fluorine as silicon tetrafluoride, applicable only to fluorides decomposed by sulphuric acid; (3) those involving the expulsion of hydrogen fluoride on treatment with sulphuric acid or potassium bisulphate; (4) methods for soluble fluorides including precipitation as lead chlor-fluoride, a volumetric titration with ferric chloride, and several other devices limited in their application to certain special fields.

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MATERIAL FOR ANALYSIS.

Calcium fluoride, prepared by treatment of sodium fluoride with calcium chloride, by conversion to calcium sulphate, gave:

CaF_2 taken	$CaSO_4$ calculated	$CaSO_4$ found	Per cent. CaF_2 present
0.0984	0.1716	0.1709	99.60
0.2917	0.5087	0.5066	99.59
		Mean	99.60

Fluorspar crystal, by conversion to calcium sulphate, gave:

Fluorspar	$CaSO_4$ calculated	$CaSO_4$ found	Per cent. CaF_2 present
0.0852	0.1486	0.1480	99.60
0.0811	0.1414	0.1407	99.50
		Mean	99.55

Sodium fluoride (Baker's C. P.) was converted into sodium sulphate and analyzed after the method employed by Treadwell and Koch,* giving

NaF = 95.10 per cent.
AlF_3 = 0.21 "
SiF_4 = 0.11 "
H_2O = 4.58 "

The Qualitative Detection of Fluorine.

With simple fluorides the ordinary etch test employing a crucible covered with a paraffined glass plate proved reliable for fractions of a milligram. With this apparatus slightly elaborated, still smaller quantities can be detected. The existing qualitative methods for fluorine in minerals and in combination with silica are unsatisfactory. The best results were obtained with the method of Casares,† involving the evolution of silicon tetrafluoride and its very delicate reaction with a drop of moisture. This would readily detect the fluorine in 1 milligram of calcium fluoride but is limited to those substances acted on by sulphuric acid.

* l. c.

† Zeit. anal. Chem., 44: 729 (1905).

Berzelius-Rose Method.

Precipitation as Calcium Fluoride.

Berzelius* originally precipitated and weighed fluorine as calcium fluoride. Rose* is responsible for the suggestion which precipitated the fluoride in the presence of carbonate to facilitate filtering. Ignition of this combined precipitate and subsequent extraction with acetic acid puts the insoluble calcium fluoride into a granular form easily filtered. This extraction has commonly been made with $\frac{3N}{2}$ acetic acid (about 10 per cent.). It has also been customary to run a control on the calcium fluoride by conversion into calcium sulphate.

Solubility of Calcium Fluoride in $\frac{3N}{2}$ Acetic Acid.

Pure calcium fluoride was first treated with $\frac{3N}{2}$ acetic acid to remove any trace of calcium carbonate or oxide and washed. Weighed amounts of this material were then treated with 10 cc. of $\frac{3N}{2}$ acetic acid on the water bath for 1 hour, filtered, washed and weighed.

Original weight	Weight after treatment	Loss
0.0797	0.0784	0.0013
0.1430	0.1413	0.0017

Mean loss per 10 cc. $\frac{3N}{2}$ acetic acid = 0.0015 gm. CaF_2†.

Loss of Calcium Fluoride on Ignition.

Some of the same calcium fluoride after treatment with acetic acid was ignited at red heat over an ordinary Bunsen flame for 1 hour:

Original weight	After ignition	Loss
0.0886	0.0870	0.0016

*l. c.

† The behavior with acetic acid has been made the basis of a very good method for the analysis of commercial fluorspar. See Bidtel: Jour. Ind. Eng. Chem., 4: 201 (1912).

It is apparent that calcium fluoride is by no means the stable substance that it is often conceived to be. The change on ignition is possibly due to formation of calcium oxide with evolution of hydrogen fluoride. It was repeatedly found that if the substance which had been ignited with consequent loss of weight was treated with hydrofluoric acid, evaporated to dryness and weighed, the original weight was restored. Thorium fluoride ignites directly to ThO_2, and cerium fluoride to CeO_2. Richards* has even found that some of the fluorides on treatment with such weak acids as lactic and butyric acids give a test for free hydrogen fluoride. Complete data upon the action of calcium fluoride toward different solvents has been presented by Treadwell and Koch,† with which these values agree. They found this substance dissolved in pure water to the extent of 0.0016 gram in 100 cc.

To determine the possible loss on ignition of calcium fluoride in contact with filter paper, a weighed amount of the pure substance free from carbonate was placed on a filter, moistened, dried and ignited.

Original weight	After ignition	Loss
0.1405	0.1401	0.0004

Determination as Calcium Fluoride in a Solution of Sodium Fluoride.

To the sodium fluoride solution was added a small amount of sodium carbonate, and the precipitate with calcium chloride filtered and treated after ignition with 10 cc. $\frac{3N}{2}$ acetic acid. The acid was evaporated to dryness, the residue taken up in hot water, filtered and weighed.

F present	F found	Loss
0.0344	0.0329	0.0015
0.0344	0.0330	0.0014
0.0344	0.0328	0.0016
0.0688	0.0664	0.0024
0.1423	0.1401	0.0022

* Analyst, 39: 248 (1914).

† l. c.

It is apparent that the error here as pointed out by Treadwell and Koch* is not proportional to the amount of fluorine present, but is an additive one depending upon the solubility of calcium fluoride in a given quantity of acetic acid. Consequently the method can, as has been suggested, be successfully employed by applying a constant correction factor. With large samples, of course, the correction is of lesser significance.

An Examination into the Delicacy of the Calcium Fluoride Precipitation.

Quantities of sodium fluoride were dissolved in 50 cc. of water, warmed, and treated with calcium chloride solution.

NaF present	F present	CaF_2 found	F found
0.0003	0.0001	No precipitate	—
0.0009	0.0004	"	—
0.0015	0.0006	"	—
0.0022	0.0009	Slight turbidity	—
0.0037	0.0016	Distinct turbidity	—
0.0066	0.0028	0.0047	0.0023

The Berzelius Method Applied to Insoluble Fluorides and Minerals.

It has been long known that simple fusion of fluorspar or calcium fluoride with sodium carbonate will not convert all the fluorine into a form in which it is soluble in water. The addition of silica to the fusion mixture does, however, bring this about. The method usually used required the fluorspar to be mixed with four times its weight of silica and six times its weight of mixed sodium and potassium carbonate. The mass is fused for 15 minutes and the blast applied for 3 or 4 minutes more. After extracting and filtering, the greater part of the silica is precipitated by evaporation with ammonium carbonate, the last traces by ammoniacal zinc oxide and the fluorine precipitated with calcium chloride in the presence of carbonate. The entire procedure is a lengthy one; its details, especially those involving the separation from silica, have been carefully investigated by

*l. c.

Seemann.* It was found preferable in the present study, to make the evaporations and precipitation in gutta percha and platinum vessels.

Obviously, in the case of minerals containing silica, less silica need be added to the flux. Reich* employs caustic soda in place of carbonate in the fusion. Many variations have been suggested to provide for the separation of phosphates, borates, etc. Seemann employs mercuric oxide instead of zinc oxide in precipitating silica, an essentially valuable method when the silica is to be weighed.

DETERMINATIONS BY METHOD OF BERZELIUS-ROSE.

CaF_2 present	CaF_2 found	Per cent. CaF_2 found
0.1098	0.0882	80.3
0.1148	0.1018	88.7
0.1648	0.1403	85.0

These low results are quite in agreement with those obtained by Seemann. Qualitative tests were applied to the residue from the original fusion and to the precipitates obtained by ammonium carbonate and zinc oxide, but the loss of fluoride could not be located. Städeler† had early suggested that an appreciable amount of the fluorine was volatilized in the fusion. To guard against this all the later descriptions of the method have cautioned against too high a temperature at fusion and have advised the use of the lower melting potassium-sodium carbonate as a flux. Seemann made elaborate examination into the possible location of this loss, could not reach any definite conclusion, but, calling attention to the existence of insoluble compounds of silicon and fluorine like $SiOF_2$, decided that the fluorine is retained in the residue from the extracted melt and in the silica precipitates in the form of such a compound.

It was thought that some of the fluorine might be lost during the evaporation, and, since the solution was strongly ammoniacal, that ammonium fluoride might be volatilized. The following blank tests were performed upon sodium fluoride, the fluorine being determined directly as lead chlor-fluoride.

*l. c.

† Jour. f. prakt. Chem., 99: 66 (1866).

	F present	PbFCl found	F found
(1)	0.0491	0.6745	0.0490
(2)	0.0430	0.5950	0.0432
(3)	0.0361	0.5047	0.0366

(1) Sodium fluoride was dissolved in 25 cc. of water and evaporated to dryness on the water bath. (2) Sodium fluoride was dissolved in 25 cc. of water and boiled vigorously to dryness. (3) A solution of sodium fluoride was treated with a large excess of ammonia and evaporated to dryness. The results show that the losses, if any, were of very small magnitude.

A series of determinations were now made to determine how much fluorine might be recovered from the silica precipitates and residue from the fusion, if the lost fluorine was really to be found there. The residue, therefore, from the extracted melt was united with the silica precipitated by ammonium carbonate and ammoniacal zinc oxide, and all refused with a fresh charge of flux. The following results were obtained:

		CaF_2 found			
Flux	CaF_2 present	1st fusion	Refusion	Total	Error
1 Na_2CO_3	0.1158	0.0988	0.0148	0.1136	—0.0022
2 NaOH	0.1237	0.0885	0	—	—
3 K_2CO_3	0.1108	0.0928	0.0159	0.1087	—0.0021
4 KOH	0.1197	0.1067	0	—	—
5 KOH	0.1193	0.1096	0.0104*	0.1200	+0.0007
6 $NaKCO_3$	0.1549	0.1400	0.0146	0.1546	—0.0003

Caustic soda and caustic potash used as fluxing agents did not recover any of the fluorine looked for. The error indicated in the other experiments is not so large as it should be, when allowance is made for the known solubility of calcium fluoride. Compensation is probably secured by very small amounts of silica or zinc oxide in the precipitates. Controls were run by conversion of the calcium fluoride into calcium sulphate with excellent agreement. Verification of results by conversion into sulphate is always reliable in the absence of phosphates. This treatment with sulphuric acid can, of course, be employed at the same time as a qualitative test for the fluorine.

While Hillebrand† had already indicated the possibility of re-

* In this refusion, sodium carbonate was employed.

† Bull. U. S. Geological Survey, No. 422 (1910), p. 187.

covery of the lost fluorine in this way by a refusion, these results serve to show that this procedure can be made to yield acceptable quantitative results. They also serve to establish the fact that the qualitative test for fluorine in complex combinations with silica can overlook quantities of several milligrams. The fluorine evidently forms a compound with the silica which is not decomposed by the sulphuric acid employed in making the qualitative test.

Much study might still be given to the process of recovering fluorine from a mineral more complex than fluorspar. Harker* observed that alumina carried considerable fluorine down with it. Much other evidence to show the difficulties caused by the presence of fluorine is not wanting.†

Different minerals appear to vary in the readiness with which they yield their fluorine on fusion. A sample of topaz gave the following:

Weight of sample	CaF_2 found		
	1st fusion	Refusion	Total
0.3910	0.1393	0.0010	0.1403

Topaz evidently yields practically all its fluorine on the first treatment. This is in strict agreement with the observations of Penfield and Minor.*

The Methods Involving the Evolution of Silicon Tetrafluoride.

Wöhler* first estimated fluorine by the formation of silicon tetrafluoride by the action of concentrated sulphuric acid upon a fluoride in the presence of some form of silica. This would be a very convenient method for the determination of the fluorine in silicate minerals, were it not for the fact that these minerals are not generally decomposed by sulphuric acid. Wöhler determined the loss in weight of his generating apparatus and called this the weight of the silicon tetrafluoride. Fresenius* absorbed

* l. c.

† See Veitch: Jour. Amer. Chem. Soc., 22: 246 (1900).
Hinrichsen: Ber., 40: 1497 (1907).
Cavaignac: Compt. rend., 158: 948 (1914).

the gas in a tube containing moistened pumice and observed the increase in weight of the tube, weighing the tetrafluoride directly. In later years both these procedures have been regarded with disfavor because quite obviously they lie open to compensating errors and involve the weighing of a complicated piece of apparatus. Hence the later methods aiming to estimate the evolved silicon tetrafluoride in some other way.

Bein* led the gas into water and estimated the silica formed according to the equation

$$3SiF_4 + 2H_2O = 2H_2SiF_6 + SiO_2.$$

This method was abandoned since the silica is not quantitatively precipitated and it is difficult to render it insoluble. Lasne* adopts the laborious method of precipitation of the fluorine from this solution as calcium fluoride after first separating the silica.

Tammann* precipitates the hydrofluosilicic acid formed, as potassium silico-fluoride in alcoholic solution, filters and titrates the precipitate with standard caustic potash, while Carnot* precipitates K_2SiF_6 by the reaction:

$$SiF_4 + 2KF = K_2SiF_6.$$

This general method has the advantage of being used in the presence of carbonates and would not be subject to the objection made against the alkalimetric methods that it would be affected by sulphuric acid carried over from the evolution flask. The handling of the gelatinous precipitate of potassium silico-fluoride is not a simple matter; it has been shown to be not completely insoluble even in 50 per cent. alcohol. Burk indicates some of the inherent difficulties of the method.* The Carnot method has invariably given lower results than the other procedures.

The alkalimetric methods are the most rapid and by far the most convenient. Penfield* receives the silicon tetrafluoride in an alcoholic solution of potassium chloride, and titrates the hydrochloric acid set free, using cochineal as indicator.

$$3SiF_4 + 2H_2O + 4KCl = 2K_2SiF_6 + SiO_2 + 4HCl$$
$$4HCl + 4KOH = 4KCl + 4H_2O.$$

*l. c.

Offermann* receives the gas in water and, using phenolphthalein, titrates according to this equation:

$$3SiF_4 + 2H_2O = 2H_2SiF_6 + SiO_2$$
$$2H_2SiF_6 + 12KOH = 12KF + 2SiO_2 + 8H_2O.$$

Both of these methods are rapid and in the past have given good results. It is worthy of note that the latter equation requires just three times the amount of standard alkali in titrating, as compared with that preceding. Hileman* gives a complete discussion of these two equations and indicates other theoretical reasons why the method of Offermann is to be preferred.

The Offermann Method.

The study of this method involves: first, the conditions governing the evolution of silicon tetrafluoride, and, second, the details of the reactions:

$$3SiF + 2H_2O = 2H_2SiF_6 + SiO_2$$
$$H_2SiF_6 + 6KOH = 6KF + SiO_2 + 4H_2O.$$

These reactions, the study of hydrofluosilicic acid and its behavior with different indicators and with different forms of alkali under varying conditions have already been carefully investigated.† Phenolphthalein has been shown to be the most convenient indicator and to give reliable results. Experimental titrations upon a solution of hydrofluosilicic acid with the aid of the hydrogen electrode served to show that this acid behaved toward caustic alkali as one of the strong acids. The following experiments were concerned more with the circumstances surrounding the evolution of the silicon tetrafluoride.

The apparatus used involved nothing new, but was an attempt to put together the best recommendations made in previous investigations. A and B contained concentrated sulphuric acid; C, soda-lime, and D, calcium chloride, these to dry the air current.

*l. c.

†Friedenthal and Salm: Zeit f. Electr. Chem., 10: 113, 341 (1904); 12: 99 (1906).
Schucht: Zeit. angew. Chem., 19: 186 (1906).
Sahlbom and Hinrichsen: Ber., 39: 2609 (1906).
Schucht and Möller: Ber., 29: 3693 (1906).

F was made from a 100 cc. distilling bulb. The entrance tube into F formed a ground joint with the neck. F was heated by means of an air bath. G was a small flask containing concentrated sulphuric acid. H, I and J served to condense any sulphuric acid carried over. H contained glass beads. I and J were empty. H and I were surrounded by cold water. K was an 8-inch test tube containing the water into which the silicon tetrafluoride was received. It was found unnecessary to employ a layer of mercury in the bottom of K. The danger of the tube becoming clogged by deposited silica was obviated by spreading the end

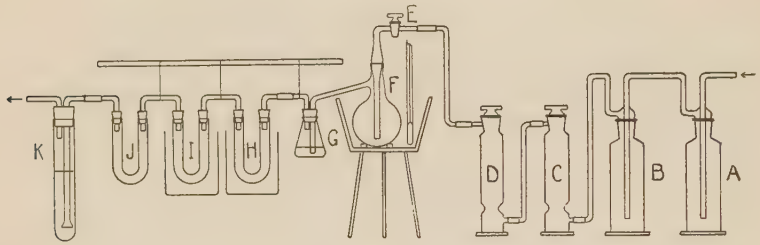

Fig. 1.

of the tube as indicated. Air pressure was furnished at A by a water pump. This was found more convenient than a gasometer and furnished a more constant stream of air than a suction pump at K. A number of preliminary experiments were made to ascertain the most suitable conditions of temperature, etc.; 0.1 gram samples of calcium fluoride were mixed with 0.5 gram powdered quartz and placed in the decomposition flask, F. A temperature of 180° was used in the preliminary experiments. These determinations were carried out in the main in accord with the detailed description of the method below.

Observations Upon the Concentration of Sulphuric Acid Required.

Determinations employing laboratory acid labelled "concentated" (analysis = 96.9 per cent. H_2SO_4):

CaF_2 present	F found	Per cent. F found	Per cent. F Theor.
0.1052	0.0425	40.4	48.52
0.1298	0.0570	43.9	

Determinations employing acid prepared by heating the above acid in a retort till about one-tenth of the volume had passed over (Method of Daniel)* (analysis = 98.6 per cent. H_2SO_4). This corresponds to "constant boiling" acid.

CaF_2 present	F found	Per cent. F found	Per cent. F. Theor.
0.0930	0.0436	46.9	48.52
0.1418	0.0678	47.8	

Seemann has shown that an acid of higher percentage formed by the addition of sulphur trioxide gives off the trioxide on heating, and is difficult to condense.

Observations on the Effect of Varying the Temperature.

	Temperature Degrees	CaF_2 present	F found	Per cent. F found	Per cent. F Theor.
1.	180	0.0930	0.0436	46.9	48.52
2.	180	0.1418	0.0678	47.8	
3.	200	0.1243	0.0589	47.4	
4.	220	0.1211	0.0570	47.1	
5.	230	0.1225	0.0583	47.6	
6.	280	0.1245	0.0564	45.3	
7.	310 (boiling point)	0.1100	0.0393	35.7	
8.	310 (boiling point)	0.1002	0.0327	32.6	

These results would indicate a temperature of 200°-220° as most desirable. In experiments 4 and 5, after titrating the solution in K, the acid in the decomposition flask was raised to the boiling point for 15 minutes and the air current continued for 1 hour longer. It was hoped in this way to obtain any fluorine which might not be expelled at 220°, but which might be driven over by boiling the acid. The water in K still showed neutral reaction. This would seem to contradict Daniel* and Hileman* who maintained the formation of an intermediate compound which was only completely broken up into gaseous silicon tetrafluoride on boiling the sulphuric acid.

Repeatedly in later determinations, the temperature of the decomposition flask was raised to the boiling point of sulphuric acid, toward the close of the operative, but no increase in the amount of silicon tetrafluoride evolved was indicated.

*l. c.

It was also noted that when heated over 280° the contents of the decomposition flask (which included always 1 gram of anhydrous copper sulphate) changed from white to a blue color, undoubtedly indicating that at this temperature even "constant boiling" sulphuric acid decomposes thus:

$$H_2SO_4 = H_2O + SO_3.$$

One of the most important conditions for the success of the method where silicon tetrafluoride is evolved has been the exclusion of every trace of moisture from the apparatus. However, it cannot be overlooked that water is one of the products of the reaction and is just as influential a factor as the concentration of the sulphuric acid used. The introduction of some dehydrating agent to take up this water is an obvious step. Drawe* suggested the use of anhydrous copper sulphate. Quantitative measurements showed:

CaF_2 present	Quartz present	Dehydrating Agent	Time Hrs.	F found	Per cent. F found	Per cent F Theor.
0.1019	0.33	None	3	0.0484	47.5	48.52
0.1243	0.50	2 grams $CuSO_4$	5	0.0589	47.4	
0.1211	0.50	2 grams $CuSO_4$	3½	0.0570	47.1	
0.0799	0.30	1 gram P_2O_5	3¼	0.0380	47.5	

The form of silica used in the formation of silicon tetrafluoride is another factor strangely affecting the reaction. Daniel* finds quartz preferable to precipitated silica and shows that quartz is more easily attacked by hydrofluoric acid than other varieties of silica. Drawe suggested the use of powdered feldspar as a "more easily combinable form" of silica. Measurements with varying quantities of each showed:

CaF_2 present	Quartz present	Time Hrs.	F found	Per cent. F found	Per cent. F Theor.
0.1243	0.50	5	0.0589	47.4	48.52
0.1211	0.50	3½	0.1570	47.1	
0.1225	0.23	4	0.0583	47.6	
0.0900	0.08	3½	0.0413	45.9	

CaF_2 present	Precipitated silica present	Time Hrs.	F found	Per cent. F found	Per cent. F Theor.
0.0859	0.20	8	0.0378	44.0	48.52

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CaF_2 present	Feldspar present	Time Hrs.	F found	Per cent. F found	Per cent. F Theor.
0.1013	0.59	2¾	0.0466	46.0	48.52
0.1168	0.50	2¼	0.0540	46.3	
0.0696	0.45	2½	0.0325	46.7	
0.0781	0.40	2½	0.0361	46.2	
0.0641	0.35	2	0.0293	45.7	
0.1547	0.20	3½	0.0719	46.4	

The use of quartz gave the most satisfactory results, while the application of silica in the form of feldspar evolved the gas in a manner which was more easily swept along to the absorption tube, with a consequently much shorter time required for the determination. When quartz was employed a continued agitation of the decomposition flask was necessary to break up the small bubbles of gas remaining collected on the surface of the sulphuric acid. When feldspar was used, the silicon tetrafluoride was evolved on heating almost as readily as is carbon dioxide from a carbonate on treatment with acid.

The Details of the Offermann Method.

The standardized procedure which the above experiments seemed to recommend and which was used in all the subsequent determinations follows: The sample of calcium fluoride weighing 0.1-0.2 gram was mixed in a mortar with three times its weight of powdered quartz. (The quartz had been strongly ignited and kept in a desiccator.) This was placed in F, about 1 gram of anhydrous copper sulphate was added and 25 cc. of concentrated sulphuric acid added. (The sulphuric acid was prepared by the method of Daniel.) With the stop-cock at E closed, the air bath was heated gradually till in ½ hour the temperature had risen to 220°. E was then opened to let an air current of about three bubbles per second pass through the apparatus and the temperature kept at 220°. Occasional shaking of the evolution flask was found desirable. When the bubbles of silicon tetrafluoride had disappeared from F, the flame was removed, the air current continued, and after about ½ hour the solution in K was titrated with N/10 KOH. The entire determination for fluorspar required about 2½ hours. A single vessel at K containing 50 cc. of water was found sufficient for the complete

absorption of the evolved gas. Another tube attached after K gave always a blank test. The apparatus employed, at the temperature employed, succeeded in completely condensing all sulphuric acid before reaching K. After using as above for twenty successive determinations, the apparatus was taken apart and the tubes H, I and J tested by washing out with a little water. That from H showed a distinct acid reaction with litmus, I was very slightly acid, while J showed a neutral reaction. A total of fifty determinations were made by this method.

The action of feldspar added to the evolution flask indicated an interesting behavior. With the hope of obtaining a form of silica which perhaps might be more perfectly adapted for use in the determination of fluorine, observations were made upon other minerals. The mineral was in each case finely powdered and intimately mixed with the calcium fluoride before this was placed in the decomposition flask.

Form of silica present		CaF_2 present	Time Hrs.	F found	Per cent. F found	Per cent. F Theor.
Calamine	0.59	0.1153	2½	0.0522	45.3	48.52
Calamine	0.41	0.0919	3	0.0418	45.5	
Leucite	0.38	0.0824	4	0.0366	44.5	
Powdered glass	0.135	0.1321	5	0.0612	46.3	
Sodium silicate	0.37	0.0961	6	0.0219	22.8	
Wollastonite	0.46	0.1138	2½	0.0366	32.1	
Wollastonite	0.56	0.1072	2½	0.0317	29.6	
Pyroxene	0.50	0.0691	2½	0.0316	45.7	

These measurements are interesting in showing the manner in which different forms of silica or at least different forms of silicate combinations may affect this reaction.

Since different forms of silica presented a varying behavior, it was sought to determine whether mineral fluorspar behaved in the same manner as precipitated calcium fluoride. The following results were obtained:

Fluorspar present	Quartz	F found	Per cent. F found	Per cent. F Theor.
0.1256	0.50	0.0592	47.2	48.50
0.1130	0.50	0.0537	47.5	
0.0783	0.50	0.0371	47.3	

CaF_2 artificial	Quartz	F found	Per cent. F found	Per cent. F Theor.
0.1243	0.50	0.0589	47.4	48.52
0.1211	0.50	0.0570	47.1	
0.1225	0.23	0.0583	47.6	

Apparently there was no difference in the reaction of these two forms of calcium fluoride. These represent the best values obtained by the Offermann method.

The fact that the best determinations by the Offermann method are low is still to be explained. The general belief has been that there is formed in the course of the reaction an oxy-fluoride of silicon, perhaps of the formula $SiOF_2$, which is in turn not decomposed by sulphuric acid. The varied behavior of the several silicates in the reaction as shown above is probably explained by the formation of such a compound. The aim, therefore, is to attain those conditions least favorable to the formation of this oxy-fluoride. Such a compound was first described by Schiff.* Daniel† has attempted to investigate the compound more intimately, but has found its isolation extremely difficult. The solid residue remaining in the decomposition flask at the conclusion of each determination was repeatedly tested for fluorine, but the methods employed failed to detect it.

Estimation of Fluorine by Precipitation as Lead Chlor-Fluoride.

This method, worked out by Starck,† takes advantage of the double halide formed on adding lead chloride to a solution of soluble fluoride, PbFCl. The method is unfortunately only applicable to soluble fluorides and these in neutral solutions. Lead chlor-fluoride is quite appreciably soluble in water, but insoluble in a saturated solution of lead chloride. A number of other soluble lead salts and other soluble chlorides were examined, but none found which would render the chlor-fluoride insoluble to the same degree. The real difficulty of the method lies in the washing of the precipitate, being a delicate matter even with the

* Lieb Ann. Suppl., IV, 27 (1865).

† l. c.

use of a Gooch crucible, and requiring the very least amount of wash water. The precipitate is dried and weighed as such in a Gooch crucible. It was found desirable to wash with ice-cold water. Satisfactory results are obtained only under carefully standardized conditions. An obvious advantage of the method is the fact that the precipitate weighed is about fourteen times the weight of the fluorine it contains. A solution of sodium fluoride was employed and treated according to the original directions.

F present	PbFCl found	F found
0.0344	0.4757	0.0345
0.0344	0.4738	0.0344
0.0492	0.6743	0.0490
0.0863	1.1941	0.0867

These figures are typical of a larger number of analyses which confirm those reported by Starck.

An "alundum" filter cone was substituted for the Gooch crucible. The washing of the precipitate on the cone was found to require a greater amount of wash water and the results were correspondingly low. It was then thought possible to use in washing the precipitate, instead of pure water, a saturated solution of lead chlor-fluoride itself. This was employed and gave more satisfactory results, as follows:

F present	PbFCl found	F found
0.0344	0.4641	0.0337
0.0344	0.4712	0.0342
0.0344	0.4744	0.0344
0.0344	0.4816	0.0350
0.0344	0.4773	0.0347

The Volumetric Precipitation of Fluorine with Ferric Chloride.

This method first used by Guyot* but elaborated by Greeff,* also applicable only to soluble fluorides in neutral solutions, involves the precipitation of the salt Na_3FeF_6 on the addition of standard ferric chloride to a solution of a soluble fluoride. This precipitation is complete in the presence of alcohol and an excess of sodium chloride. The end point is read by the use of thiocyanate as indicator and absorption of the red thiocyanate color

*l. c.

in an ether layer. A standard solution of ferric chloride was used of such value that 1 cc. = 0.00267 gram of fluorine. Bellucci* has shown the effect of varying the quantity of pure sodium chloride present. The method was applied to a solution of sodium fluoride according to the recommendations of Greeff, and showed reliable results.

F present	NaCl present (grams)	F found
0.0344	1	0.0339
0.0344	1	0.0339
0.0993	2	0.0995
0.0585	1	0.0582

In several determinations the ordinary sodium chloride found in the laboratory was substituted for the C. P. salt, giving results as follows:

F present	NaCl present (grams)	F found
0.0344	2	0.0331
0.0543	2	0.0281
0.0688	2	0.0585
0.0866	2	0.0643
0.1094	3	0.1057

These values showed a very wide range from the true figures; they do serve to show, however, that the influence of slight amounts of impurities present in the sodium chloride was considerable.

In place of sodium chloride, pure potassium chloride was used, giving:

F present	KCl present (grams)	F found
0.0301	4	0.0304
0.0343	4	0.0341
0.0344	4	0.0347
0.0387	4	0.0387
0.0585	4	0.0587
0.0619	4	0.0630

Potassium chloride seemed to recommend itself quite as well as sodium chloride.

Attempts were made to apply this volumetric method to the analysis of fluorspar. The powdered mineral was fused with silica and sodium-potassium carbonate. The silica was precipi-

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tated by ammonium carbonate and ammoniacal zinc oxide. The resulting solution was neutralized, diluted to 30 cc., 4 grams of potassium chloride added, and titrated with standard ferric chloride solution. No satisfactory end point could be obtained.

The Guyot-Greeff volumetric method seems to recommend itself highly for simple solutions of sodium fluoride, but to fail when other substances are present.

Precipitation of Fluorides as Calcium Fluoride in the Presence of Calcium Oxalate.

Starck and Thorin* have presented this modification suggesting the addition of a known volume of standard ammonium oxalate before precipitating with calcium chloride, with the idea that the presence of oxalate would render the calcium fluoride precipitate more insoluble and at the same time aid in its filtration. The combined precipitates were filtered on to a Gooch crucible, dried and weighed according to the original directions. The known weight of the calcium oxalate was subtracted from the total. Results:

F present	CaC_2O_4 present	$CaF_2 + CaC_2O_4$ found	CaF_2 found	F found
0.0344	0.1097	0.1787	0.0690	0.0336
0.0344	0.1097	0.1786	0.0689	0.0335
0.0344	0.1097	0.1796	0.0699	0.0340

It was found preferable to determine the strength of the ammonium oxalate solution by precipitation and weighing as calcium oxalate rather than by titration with permanganate. The numerical results of Starck and Thorin are verified, but the combined precipitate of calcium fluoride and oxalate was found extremely difficult to filter and handle, contrary to the observations of the original proposers of this modification. The method is obviously limited to the estimation of fluorine in neutral solutions of soluble fluorides only, in the absence of most other substances.

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Precipitation as Thorium Fluoride.

Thorium fluoride is precipitated in gelatinous form, but becomes rapidly granular on standing, making it in consequence easy to filter. A further advantage lies in the fact that simple ignition transforms it to dioxide in which form it can be weighed. The fluoride must be precipitated moreover in strictly neutral solutions. The best results obtained were far from satisfactory.

F present	F found
0.0688	0.0661
0.0344	0.0368
0.0344	0.0329

Some doubt was felt whether simple ThF_4 could be precipitated from a solution of sodium fluoride without being accompanied at the same time by some Na_2ThF_6. A solution of about 0.5 gram of sodium fluoride was treated with an excess of thorium nitrate in neutral solution. The washed precipitate was dissolved in acid, the thorium precipitated by ammonia, and from the filtrate a small amount of sodium chloride was obtained.

The Colorimetric Estimation of Fluorine.

A number of characteristic reactions for the metals are known upon which the presence of fluorine exercises an inhibitory influence. Steiger's method,* improved by Merwin,* takes advantage of the color produced on treating a titanium solution with hydrogen peroxide. Fluorine tends to destroy this color. This "fading" effect can be readily measured by comparing the depth of color of two equivalent titanium solutions, one of which contains the fluorine, while the other does not. This indirect method was worked out in the U. S. Geological Survey for analysis of fluorine-containing minerals and, as pointed out by the authors, is only applicable to fluorine in very small amounts. They also emphasize the necessity of each analyst carefully setting for himself standard conditions and developing a factor which shall satisfy his own conditions of operation.

To calculate the factor: About 0.02 gram of calcium fluoride was taken, fused with silica and 1 gram of sodium carbonate,

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extracted with water and the silica precipitated with ammonium carbonate. To the solution were added 3 cc. of hydrogen peroxide, 10 cc. of titanium sulphate (= 0.01 gram TiO_2), 6 cc. of sulphuric acid and the whole diluted to 100 cc. Its depth of color was compared by means of a Duboscq colorimeter with another titanium solution prepared under the same conditions, but containing no fluorine. A blank reading to provide for the influence of sodium sulphate gave the number, 103. Substituting in the formula, $\frac{R - 103}{X}$ = grams of fluorine, the following readings gave:—

Calcium fluoride	F present	Ratio R	Factor X calculated
0.0142	0.0068	120	2500
0.0182	0.0088	125	2500

Using this formula, $\frac{R - 103}{2500}$, the following results were obtained:

Calcium fluoride	F present	Ratios	F calculated
0.0230	0.0115	132	0.0116
0.0389	0.0188	150	0.0188

These results show that under standardized conditions reliable results can be expected. A less concentrated titanium solution provides for still smaller amounts of fluorine. On a qualitative basis alone, the method stands as probably the only satisfactory means of detecting in a silicate amounts of fluorine less than a milligram.

Influence of Fluorine on the Ferric Thiocyanate Reaction.

Fluorine likewise produces a fading effect upon the color produced between a ferric salt and ammonium thiocyanate. The red color is more suitable for comparison than the titanium color and it was thought would lend itself to the detection of larger amounts of fluorine. A preliminary study was made into the extent to which the thiocyanate color would be affected by reagents other than fluorides.

Solutions were prepared as follows: A solution of alum (1 cc. = 0.01 gram of Al_2O_3), a solution of sodium silicate (1 cc. =

0.01 gram of SiO_2), a solution of microcosmic salt (1 cc. = 0.005 gram of P_2O_5). The effect of each of these common constituents of rocks, *i. e.*, Al_2O_3, SiO_2, P_2O_5, was tried in turn upon a solution containing 10 cc. of ferric chloride (= 0.03 gram Fe_2O_3) and 5 cc. of 5 per cent. solution of ammonium thiocyanate, diluted to 50 cc., and compared with a standard prepared under similar conditions.

Influence of Al_2O_3:

	1 cc.	2 cc.	5 cc.	10 cc.
Ratios	112	150	271	350

Influence of SiO_2:

	3 cc.	10 cc.	20 cc.
Ratios	100	140	148

Influence of P_2O_5:

	1 cc.	2 cc.	3 cc.
Ratios	114	226	Decolorized

Influence of Na_2CO_3 neutralized with HCl:

	1 gram	3 grams	5 grams
Ratios	102	113	125

Influence of sodium fluoride:

F present	0.0004	0.0007	0.0010	0.0014	0.0018
Ratios	124	128	142	161	166

These last values arrange themselves along a curve which could be used in reading the unknown amount of fluorine present necessary to produce a given fading effect, but the decided deleterious influence of the phosphorus, alumina, etc., which usually accompany fluorine in minerals shows the reaction not well adapted to such a field. It was further determined that the thiocyanate color is not a permanent one. Exposed to light, a solution was found to lose one-half its depth of color in 48 hours.

On the Behavior of Fluorspar and Cryolite in Hydrochloric Acid Gas.

The halogens, chlorine, bromine and iodine when passed through a tube over samples of fluorspar heated to redness in a boat produced no reaction with the mineral. It is known that hydrochloric acid gas will transform sodium fluoride to sodium

chloride. The effect of this gas was tried upon mineral fluorspar.

The powdered fluorspar was placed in a platinum boat and heated in a fairly rapid stream of hydrogen chloride for 5 hours. To determine if the decomposition was complete, the contents of the boat after the operation were treated with water, when the calcium chloride formed dissolved. A high temperature was found necessary. At 350° the mineral was only very slightly decomposed. The amount of decomposition increased with higher temperature. At 500° after most of the mineral had been acted upon the resultant calcium chloride fused, occluding in the fused mass undecomposed mineral and the action ceased. At 450° the action was extremely slow and after 8 hours showed still only partial decomposition. None of eight different samples, weighing 0.1 to 0.2 gram, subjected to hydrogen chloride gas were more than partly acted upon. Apparently that temperature could not be found, high enough to cause complete reaction with hydrochloric acid, and low enough to prevent fusion of the calcium chloride.

The mineral cryolite behaved in a different manner. A sample of 0.1380 gram heated at 600° in hydrogen chloride for 6½ hours left a residue weighing 0.0875 gram which dissolved in a few drops of water to a clear solution. A second sample of 0.1252 gram at 650° for 6 hours left a residue of 0.0823 gram and dissolved completely. The aluminum chloride formed volatilized completely and carried with it some of the sodium chloride.

The Decomposition of Topaz by Calcium Carbonate.

Lenz,* desiring to estimate the amount of fluorine in an organic compound, heated the substance with calcium oxide and after extraction with dilute acetic acid weighed calcium fluoride. Kessler* applied this method to sodium and ammonium fluorides. The principle employed recalled the J. Lawrence Smith method for alkalies; an attempt was made to use this to aid in the decomposition of fluorides not decomposable by sulphuric acid. A sample of topaz, finely powdered, was intimately mixed in a

*l. c.

mortar with ten times its weight of calcium carbonate and three times its weight of ammonium carbonate. This was heated in a covered crucible for 15 minutes with a small flame, and for 15 minutes more to intense redness. The fluorine, it was thought, was now entirely transformed into calcium fluoride and the mass free from carbonate. It was powdered and placed with anhydrous copper sulphate and sulphuric acid in the apparatus for estimating fluorine by the Offermann method. The conditions of preliminary ignition were varied in a number of trials, but the best results were always low:

Topaz present	F found	Per cent. F found	Per cent. F present
0.2380	0.0414	13.9	17.48*
0.2487	0.0369	14.8	
0.2240	0 0321	14.4	
0.2449	0.0352	14.4	

This procedure failed to produce a successful method for fluorine. The ignition with calcium carbonate evidently led to the formation of calcium silicate. It is interesting to note that strikingly low results were likewise obtained when this substance in the form of wollastonite was applied to the Offermann method.

Additional Observations.

It remains possible that some other metallic fluoride than those usually used might be adapted to an analytical method. The existing data upon the properties and solubilities of the fluorides is extremely meager. The fluorides of most of the metals were examined. Many of those generally regarded as insoluble were found not quantitatively insoluble, while practically all were formed as gelatinous precipitates quite impossible to filter and wash. Barium fluoride has been used by Gautier† in a special method for fluorine in mineral water. Cerium fluoride seemed to recommend itself, since on ignition it is transformed to the dioxide. It was found necessary to precipitate the fluoride of cerium in a solution absolutely neutral. The precipitate formed was almost colloidal and the weights of cerium oxide obtained always low.

* Determined by the method of Berzelius-Rose.

† l. c.

There are other volatile compounds which might be employed other than silicon tetrafluoride. Jannasch* expels as hydrofluoric acid and collects in alkali; an elaborate piece of platinum apparatus is required which is almost prohibitive. The fluorine is then precipitated and weighed as calcium fluoride. The "etch" methods likewise involve the evolution of hydrogen fluoride. The consequent measurement in some way of this etching effect is hardly to be favored as an analytical method.

Boron fluoride is formed upon treating a fluoride with sulphuric acid in the presence of boric anhydride. In attempting to carry this out under conditions corresponding to those of the Offermann method for silicon tetrafluoride, it was found that silicon fluoride was likewise formed in the glass decomposition flask, and carried along with the boron fluoride to the absorption tube forming both H_2SiF_6 and HBF_4, incapable of being estimated by a simple titration. Hydrofluoric acid likewise forms a volatile ethyl ester which might be applied if some simple method of forming it analytically could be found.

Conclusions.

1. The methods for fluorine have been reviewed.

2. It has been shown that by means of a refusion with carbonate all the fluorine in silicate minerals can be accounted for by the Berzelius-Rose method.

3. The conditions have been indicated according to which the best results can be obtained in the volatilization of silicon tetrafluoride by the Offermann method. This method is to be preferred for the direct estimation of fluorine in fluorspar.

4. Soluble fluorides can be most accurately determined by precipitation as lead chlor-fluoride.

5. The only satisfactory method of determining and detecting fluorine in small quantities in minerals is the colorimetric method of Steiger-Merwin.

*l. c.